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Some Computational Treatments

by

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Detonation Initiation and Sensitivity in Energetic Compounds: Some Computational Treatments

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Abstract

The initiation of detonation in an energetic compound, and its sensitivity to external stimuli, involves a complicated interaction of such determinants as molecular structure, crystal properties and physical state. There have been numerous computational analyses of the roles of the first two of these factors. Molecular dynamics techniques have been used extensively to simulate the initiation and propagation of detonation in model lattices, as well as to study processes (e.g. energy transfer) in actual energetic compounds. There have also been many investigations of possible relationships between impact and shock sensitivities and various molecular properties, ranging from stoichiometries to C-NO₂ and N-NO₂ bond strengths to molecular surface electrostatic potentials. This chapter presents an overview of some of these computational treatments, with the objective of conveying a sense of what has been and is being done, its limitations, and its successes.

1. Introduction

A continuing major concern in the area of energetic materials (e.g. explosives and propellants) is their vulnerability to explosion caused by accidental external stimuli. Such stimuli can include impact, shock, friction, heat and electrostatic charge.¹ The degree of vulnerability is commonly termed the "sensitivity" of the material, as it shall be in this chapter; it should be noted, however, that some researchers, especially in the United Kingdom, use the word "sensitiveness" when the stimulus is accidental and "sensitivity" when it is intended.²

Upon initiation from an external source, an energetic compound - which is necessarily metastable - undergoes rapid chemical decomposition with the release of a large amount of energy. As has been pointed out, "All explosives are, intrinsically, sensitive to impact and shock."³ In designing and evaluating new energetic materials, therefore, the objective is the somewhat contradictory one of maximizing energetic performance while minimizing sensitivity.⁴

There have been very extensive efforts, over a period of many years, to understand the factors that determine sensitivity, especially toward impact and shock, and to develop a predictive capability. However the initiation of decomposition in an energetic compound involves a complex interplay of various elements (including its molecular structure, its crystal properties and its physical state), some of which can be quite variable. Thus it can even be difficult to achieve reproducible measurements of sensitivity.^{1,5,6}

Nevertheless, some significant progress has been made in relating sensitivity, qualitatively and even quantitatively, to its various determinants. Some of the studies focusing upon the effects of molecular structure shall be mentioned later in this chapter. Our initial emphasis shall be upon efforts to understand how crystal properties affect impact and shock sensitivities.

2. Background

Early experimental work supported the idea that impact-initiated explosions can be viewed as thermal decomposition processes.⁷⁻⁹ Bowden and Yoffe introduced the concept of "hot spots",⁸ which continues to be a key element in the interpretation of explosive initiation.^{2,10-19} Hot spots are small regions in a crystal in which thermal energy generated by impact or shock is localized. This may be channeled into molecular vibrational modes and, if sufficient, lead to bond-breaking and the beginning of decomposition.¹⁰⁻¹⁵ (It has recently been suggested that the vibrational properties of nitro groups, which are a typical component of energetic compounds, are particularly well suited for localizing transferred vibrational energy.^{14,15}) While the initial bond-breaking is necessarily endothermic, it is followed by exothermic chemical reactions which produce energy that sustains and expands decomposition. The hot spot must be large enough and hot enough that this is not quenched by dissipation of heat through thermal diffusion, and it must be sufficiently long-lived that the reactions are well underway.^{2,8,16-19} Bowden and Yoffe concluded that hot spots need to have dimensions of approximately 0.1 to 10 μm , temperatures greater than roughly 700 K, and durations of 10^{-5} to 10^{-3} seconds.^{8,16}

It seems to now be widely accepted that both impact- and shock-initiated explosions can be regarded as thermal decompositions.^{13,17,20-22} although other views have been expressed^{23,24} and key details are different: impact produces pressures of 7 to 15 kbar and heating over 200 to 300 μs , in contrast to 30 to 200 kbar and $\leq 1 \mu\text{s}$ for shock.²⁵ Recent work suggests that the properties of the hot spots resulting from the two types of stimuli are also different, those due to shock being smaller, hotter and of shorter duration.¹⁸ (As might be anticipated, there is an inverse relationship

between hot spot temperature and size.²⁶) However a general correlation has been demonstrated between measured impact and shock sensitivities.²⁷

What gives rise to hot spots? Why does externally-introduced energy concentrate in certain small regions of the crystal? Hot spots are commonly attributed to the presence of defects in the crystal:^{2,17,19,28-30} these might include lattice vacancies, interstitial occupancy, molecular rotations, edge and screw dislocations, twinning, and other possible imperfections. Such defects produce strain in the crystal. The relief of this strain by externally-introduced energy (via crystal relaxation and rearrangement) results in the disproportionate localization of energy in the neighborhood of the defect, creating a hot spot^{28,31-33} and leading to vibrational excitation^{33,34} and chemical reaction.^{35,36}

It should be noted, however, that the essential role of defects is not universally accepted. There are molecular dynamics studies which suggest that detonation can occur even in a defect-free crystal.³⁷⁻³⁹ It has also been proposed that hot spots can develop if there is an efficient channel for transferring energy into specific anharmonic vibrational modes,¹³⁻¹⁵ even without the intervention of defects, although their presence may facilitate the transfer.^{40,41}

3. Molecular Dynamics Studies

The velocity with which a detonation travels through a typical explosive is 50 to 90 A/ps.^{1,6} As was pointed out by Brenner *et al.*,⁴² such a process is very appropriate for study by molecular dynamics simulation. This has indeed come to be an important tool for elucidating the role of crystal properties in the initiation and propagation of energetic material detonation. In much of this work, the focus has been upon the process itself - the movement of a shock wave through a crystal, the transfer of energy and the role of structural defects - and a model system was used, e.g. a monatomic or diatomic lattice. More recently, however, efforts are being made to simulate actual energetic compounds and, eventually, their initiation and detonation. This poses the challenge of developing appropriate treatments of the various inter- and intramolecular interactions that are involved. Both types of studies shall be briefly surveyed.

3.1. Model Systems

The early work of Karo *et al.*,⁴³ who simulated a shock wave in a two-dimensional monatomic lattice, has subsequently been extended and expanded by many others. Some representative investigations will be mentioned.

32.44

Monatomic lattices continue to be attractive and convenient systems to study, despite their obvious limitations as models for actual energetic compounds. Sinkovits *et al* used two-dimensional square and hexagonal arrays of 4000, 8000 or 16000 point particles interacting through a Lennard-Jones potential.⁴⁴ A shock was induced by the impact of a rapidly-moving "plate" composed of these particles. The resulting disruption of the lattice was found to be considerably greater when defects (primarily vacancies) were present. The latter were also the sites for the development of thermalized, fluid-like regions (hot spots).

Many simulations have focused upon various types of idealized molecular lattices. For example, a popular approach has been to represent the nitromethane molecule, H₃C-NO₂, by

37-39.45

means of the diatomic C-N. The interactions within and between these CN units were described by Lennard-Jones and/or Morse potential functions. These were parametrized in various ways, including *ab initio* calculations and imposing the requirement that the speed of sound through the crystal be reproduced in reasonable agreement with experiment. Shock waves were initiated by applying impacts at one end of the system. Several ingenious techniques have been devised to simulate the effects of the exothermic chemical reactions that follow the initial

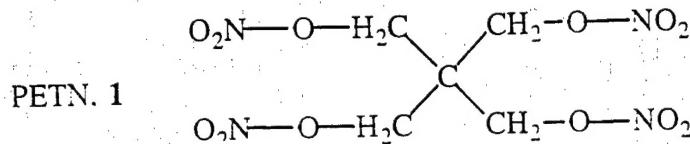
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endothermic bond-breaking. Maffre and Peyrard did this by expressing their intramolecular C-N potential as the difference between two Morse functions,³⁸ such that the initial input of energy needed to break the C-N bond is followed by a greater release of energy at large C-N separations. A common feature of the results of these "nitromethane" studies is that a detonation wave can be generated even in the absence of lattice defects, although their presence may enhance the process.

In another simulation of a diatomic lattice,³⁴ using harmonic intramolecular and Morse intermolecular potentials, a cylindrical void was positioned transverse to the direction of the shock wave. When the latter had sufficient velocity, a turbulent structural collapse was observed near the void, with a transfer of energy into the internal vibrational modes of the nearby molecules.

The effects of voids were also investigated for systems of 512 eight-atom cubic molecules, with all interactions represented by Morse potentials.^{32.33} A shock wave was generated by rapid compression of the lattice. It produced structural relaxation near the vacancy, with an accompanying increase in the local kinetic energy (a hot spot) and vibrational excitation. Another significant finding came in comparing the results of compressions in the [100] and [110] crystallographic directions;³² the energetic effects, such as the increase in kinetic energy, were greater in the latter instance. Earlier, structural analyses of pentaerythritol tetranitrate (PETN, 1 and nitromethane had indicated certain directions to be favored for detonation.⁵⁰ Such predictions

are consistent with the orientation-dependent sensitivity that has been observed experimentally for PETN^{51,52} and for nitromethane.⁵³⁻⁵⁵

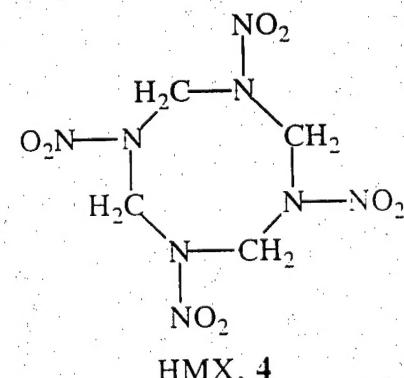
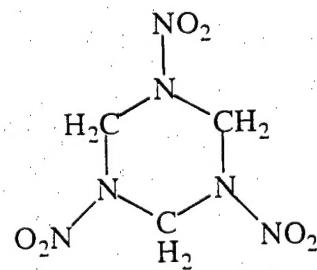
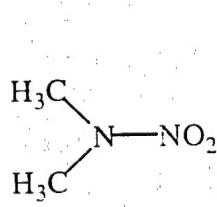


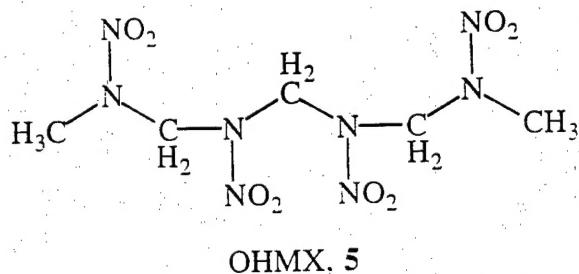
Given the unrealistic features of model systems such as have been described, and the inconsistencies between various treatments, it is not surprising that different studies have sometimes led to contradictory conclusions concerning the relationships between detonation propagation, crystal disruption, vacancies and hot spots. Overall, however, these simulations have complemented experimental work in developing the current understanding of explosive initiation, hot spot formation, the role of defects, detonation propagation, vibrational excitation, etc.

Nevertheless, it is clear that the amount of insight and useful information to be obtained from idealized model systems is limited. The next step then is to move on to simulations of actual energetic compounds. Some efforts in this direction will be summarized in the next section.

3.2. Actual Energetic Compounds

In order to realistically simulate an energetic compound, it is necessary to deal with both the intermolecular interactions in the crystal and the intramolecular interactions within each molecule. A first step can be to simulate the isolated molecule, thus requiring only intramolecular potential functions. This has been done for several nitramines, including dimethylnitramine (**2**), 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX. **3**), 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX. **4**) and 1,7-dimethyl-1,3,5,7-tetranitrotrimethylenetetramine (OHMX. **5**).⁵⁶⁻⁵⁹





Thompson and his collaborators studied dimethylnitramine and RDX, **2** and **3**, treating bond-stretching with Morse functions, angular motions as harmonic, and torsion with trigonometric potentials.⁵⁶⁻⁵⁸ Parameters were based largely on spectroscopic and computed data. Lennard-Jones potentials were used for non-bonded interactions. The simulation of **2** focused upon intramolecular vibrational energy transfer from excited CH₃ stretching modes.⁵⁶ This was found to be rapid and irreversible, and predominantly to the other CH₃ group. This observation, which may of course be relevant to the widely-used explosives RDX and HMX, **3** and **4**, is in contrast to the more recent emphasis placed upon the nitro group as having an enhanced capability to localize transferred vibrational energy.^{14,15} However the latter refers to energy from an external source, not intramolecular transfer. The simulations of RDX were designed to investigate the effect of a solvent (xenon) on chair → boat ring inversion⁵⁸ and to model its unimolecular dissociation.⁵⁷ Two avenues were explored for the latter process: simple N–N bond scission to release NO₂ and concerted triple C–N rupture to form three molecules of H₂C=N–NO₂. The results, in terms of the branching ratio between the two paths and the product energy distributions, are in reasonable agreement with those of a molecular beam study, which concluded that the concerted ring fission dominates.⁶⁰

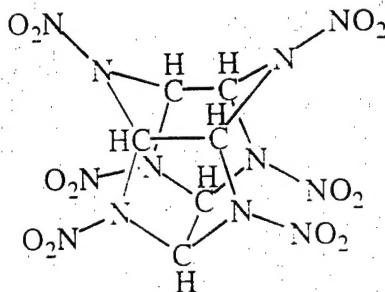
The work by Kohno *et al* dealt with all four of the nitramines **2** - **5**.⁵⁹ While each simulation treated only one molecule, efforts were made to take at least some account of crystal effects, for example by using the crystallographic molecular starting geometry. The code was CHARMM22,⁶¹ which employs primarily harmonic bond and angle potentials, with Lennard-Jones and coulombic functions for non-bonded interactions. Force constants and atomic charges were obtained mainly through correlated *ab initio* calculations. An important motivation for this study was the recently-proposed hypothesis (to be discussed further in section 4) that nitramine impact sensitivity is related to the compression of the N–N bond in the crystal compared to the gas phase.^{62,63} The oscillatory behavior of the various bonds was examined and compared for the molecules in their crystal or their gas phase optimized geometries, and intramolecular vibrational energy transfer between N–NO₂ moieties was investigated. It was concluded that in detonation

initiation, the function of the compressed N-N bonds in crystalline nitramines, especially cyclic ones, is to concentrate and store energy for the process.

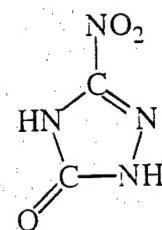
A very recent series of studies has approached the problem of simulating actual energetic compounds from a different direction.⁶⁴⁻⁶⁷ A crystal lattice was built up from the appropriate molecules, but the structures of the latter were held fixed (i.e. rigid molecules). Thus only intermolecular interactions had to be considered. For RDX, 3, the lattice consisted of 216 molecules in 27 unit cells.⁶⁴ The intermolecular potential included a coulombic term for electrostatic interactions and a Buckingham-type van der Waals term (exponential repulsion and $1/r^6$ attraction). Atomic charges were obtained by fitting to the separately-computed molecular electrostatic potential of RDX. The Buckingham parameters were optimized to reproduce experimental crystal packing data. Simulations were performed at six temperatures ranging from 4.2 K to 325 K. In order to test the effectiveness of the procedure, which was a primary objective, several crystal properties were calculated, including structural features and coefficients of thermal expansion. The results were in satisfactory agreement with experimental data.

This success prompted applying the same general approach to three polymorphic forms of 2,4,6,8,10,12-hexanitrohexaazaisowurtzitane (HNIW, 6),⁶⁶ a very energetic new explosive. The parameters used for the Buckingham potential were the same as for RDX: atomic charges for the coulombic interaction were determined by fitting to the molecular electrostatic potential of one of the HNIW polymorphs. The lattice was composed of either 12 or 27 unit cells, each with 4 molecules. Crystal structures were again well reproduced; thermal expansion coefficients were computed but no experimental values were available for comparison. Finally, the procedure was extended to three polymorphs of HMX, 4, with similarly good results.⁶⁷

A slightly different technique was used for the compound 5-nitro-2,4-dihydro-3*H*-1,2,4-triazol-3-one (NTO, 7).⁶⁵ In addition to the coulombic term, a Lennard-Jones potential described non-bonded interactions, with a separate function ($1/r^{12}$ repulsion and $1/r^{10}$ attraction) for hydrogen bonding. These were parametrized from earlier work or by fitting experimental data. Simulations were carried out at temperatures ranging from 4.2 K to 400 K for a lattice of 45 unit cells, each having four molecules. Crystal structural features were predicted with satisfactory accuracy: thermal expansion coefficients were calculated but comparison to experimental data was again not possible.



HNIW, 6



NTO, 7

The purpose of these studies of crystal lattices composed of rigid molecules was to develop the approach being used and to evaluate its effectiveness in reproducing certain crystal properties. In no instance was shock or impact simulated. While notable success has been achieved in describing the crystals of actual energetic compounds, providing support for the validity of the intermolecular potentials, there remains the limitation represented by the rigid molecule assumption. This precludes excitation of molecular vibrational modes, bond-breaking, and other key features of detonation initiation. There is a need for the next step, which is to combine the two approaches that have been described in this section on actual energetic compounds. This requires realistic potential functions that treat both inter- and intramolecular interactions.

This has recently been done for nitromethane, although in the liquid rather than the solid state.^{68,69} The code CHARMM was used,⁶¹ which treats stretching and most angular motion as harmonic, and non-bonded interactions with Lennard-Jones and coulombic functions. Force constants and atomic charges were obtained by density functional calculations, with the special feature that these were repeated, for small clusters of molecules, several times during the course of the simulation. This was done in an effort to take account of intramolecular changes resulting from intermolecular interactions. The objectives of this work were to obtain information about the structure of liquid nitromethane, and to try to reproduce the observed effects of increased pressure and temperature upon the molecular vibration frequencies. The agreement was good for CN and NO₂ stretching, but poorer for CH₃ stretching, possibly because the force field did not properly reflect intermolecular hydrogen bonding.

None of the molecular dynamics simulations that have been described have sought to actually correlate or predict the sensitivities of real energetic compounds, although that is certainly an eventual objective. There have, however, been some theoretical treatments that do succeed in relating sensitivity to dynamic crystal effects, although not through simulations. Thus, Fried and Ruggiero¹⁴ and McNesby and Coffey⁷⁰ developed separate procedures for calculating the rate of transfer of energy from lattice vibrations to internal molecular vibrational modes, e.g. bond stretching. Experimental input was required in both cases, neutron scattering data to determine the

density of vibrational states in one instance¹⁴ and Raman spectra to obtain the solid-state vibrational energy levels in the other.⁷⁰ The energy transfer rates were shown to correlate with impact sensitivities within two series of seven compounds.

4. Molecular Structure Correlations

The preceding section has described molecular dynamics approaches which have the ultimate aim of realistically simulating detonation initiation and propagation in energetic compounds, both to increase our understanding of these processes and also to provide insight into the crystal factors that affect sensitivity. As was pointed out earlier, molecular structure also plays an important role in determining sensitivity. Given the complexity of the crystal phenomena that are involved, it might be anticipated that considerations of molecular structure alone would not be productive. On the contrary, however, some rather good correlations have been developed between impact or shock sensitivity and various molecular properties, generally within a given class of compounds.

4.1. Stoichiometry

It seems remarkable that it has proven possible to quantitatively relate impact sensitivity to molecular stoichiometry alone.^{5,10,71-75} Probably the best known is Kamlet's work,^{5,10,73} which showed that the sensitivities of nitroaromatics, nitroaliphatics and nitramines (treated separately) correlate with the "oxygen balance," which is basically a measure of the oxygen available in the molecule relative to what is needed to convert all hydrogens to water and carbons to carbon monoxide. In general, impact sensitivity tends to increase with the oxygen balance; however Bliss *et al* feel that this is coincidental, and that oxygen balance is more relevant to propagation than to initiation.⁷⁶ A more positive view was offered by Mullay, who showed that oxygen balance can related roughly to molecular electronegativity.⁷⁷

4.2. Trigger Linkage

Kamlet also emphasized the concept of a "trigger linkage," a bond whose rupture is a key step in detonation initiation.^{10,73} (He further suggested that rotation around this bond can act as a desensitizing energy sink, absorbing energy that might otherwise go into bond-stretching and promote cleavage;¹⁰ thus it is desirable to avoid steric hindrance of such rotation.) While trigger linkages are believed to often be C-NO₂ or N-NO₂ bonds,⁷⁸⁻⁹² this is not invariably the case.^{4,76,93,94} For example, Kamlet and Adolph were obliged to establish a separate oxygen

balance correlation for nitroaromatics having a CH-containing substituent *alpha* to a nitro group. indicating a special significance for the C-H bond: experimental studies are consistent with this interpretation.^{25,95,96}

There have been a number of efforts, with some degree of success, to relate impact or shock sensitivities to computed properties of C-NO₂ and N-NO₂ bonds. Several of these have focused upon some measure of bond strength, such as the activation barrier to homolysis.^{97,98} the bond length,^{99,100} and various functions of the carbon and nitrogen atomic charges.^{99,101,102}

Most of these correlations were limited to a specific type of compound, e.g. nitroaromatics; however Owens was able to include C-NO₂, N-NO₂ and even O-NO₂ bonds of nitroaromatics, nitramines, a nitroaliphatic and even a nitrate ester in his impact sensitivity vs. homolysis activation barrier relationship.⁹⁷ On the other hand, no general correlation was found between the impact sensitivities of a group of nitroheterocycles and their C-NO₂ dissociation energies.¹⁰³ Brill and James have argued that the differences in the barriers to C-NO₂ homolysis among nitroaromatics are not sufficient to explain the range in sensitivities.¹⁰⁴

Some interesting variations on the theme of the trigger linkage have been introduced. Delpuech and Cherville proposed that shock sensitivities in nitroaromatics, nitramines and nitrate esters can be related to the changes in polarities of the C-NO₂, N-NO₂ and O-NO₂ bonds in going from the ground to electronically-excited states of the molecules.¹⁰⁵ The idea of electronic excitation playing a role in detonation initiation continues to be invoked on occasion:^{106,107} for example, Sharma *et al* correlated impact sensitivities with valence electron promotion energies obtained from photoelectron spectra.¹⁰⁸

A particularly interesting concept is one that was already mentioned earlier. Kohno *et al* have observed that the N-NO₂ bonds in several nitramines are 0.05 to 0.08 Å shorter in the crystal than in the gas phase,^{59,62,63} the latter generally being obtained computationally. Limited evidence suggests that this is not the case for the other bonds in these molecules. Kohno *et al* feel that the compressed N-NO₂ bond in the crystal represents a source of strain. (In the context of the discussion in section 2, it could be viewed as a crystal defect.) Their molecular dynamics simulations, summarized briefly in section 3.2, provide some support for their arguments. Kohno *et al* believe that the extent of N-NO₂ shortening in the crystal compared to the gas phase is closely related to the impact sensitivity of the compound, and they do show reasonable qualitative agreement between the two for a series of seven systems.

4.3. Molecular Surface Electrostatic Potential

An approach that emphasizes the entire molecule rather than a specific bond involves the electrostatic potential computed on the molecular surface. We have found that a variety of condensed phase properties that depend on molecular interactions (e.g. enthalpies of vaporization, sublimation and fusion, boiling points and critical constants, solubilities and solvation energies, partition coefficients, diffusion constants and viscosities, etc.) can be represented analytically in terms of quantities that characterize the surface potential: its maxima and minima, positive and negative averages and variances, and average deviation.¹⁰⁹⁻¹¹¹ (The molecular surface is taken to be the 0.001 au contour of the electronic density.¹¹²)

This type of analysis has been extended to the correlation and prediction of impact sensitivities.^{4,113,114} We have found that energetic molecules differ from what is normally observed in that the positive surface potentials tend to be stronger (i.e. larger in average magnitude) than the negative. For molecules in general, the reverse is typically true. We have shown that the extent of the anomalous imbalance between the strengths of the positive and negative surface potentials, which is characteristic of energetic molecules, can be quantitatively related to impact sensitivity, within series of nitroaromatics, nitroheterocycles and nitramines.^{4,114}

4.4. Other Molecular Approaches

There have also been other sensitivity correlations proposed that directly invoke properties of the entire molecule. Fukuyama *et al* focused upon the energetics associated with activation and decomposition,¹¹⁵ while Belik *et al* used an average molecular "resonance energy" as well as stoichiometric considerations.¹¹⁶ The Quantitative Structure-Property Relationship methodology has also been utilized. Impact sensitivity was expressed in terms of eight molecular descriptors, which include the oxygen balance and functions of atomic radii, charges and molecular topology.¹¹⁷ Using regression analysis and a data base of 78 compounds of various chemical types, a relationship was obtained that reproduced their sensitivities with generally good accuracy.

5. Summary

Initiation of detonation in energetic compounds involves a complicated interaction of crystal, molecular and physical factors. Efforts to develop a capacity for predicting and possibly modifying the sensitivities of compounds to unintended stimuli have proceeded along both experimental and theoretical lines. Our aim in this chapter has been to present an overview of some of the computationally-based approaches, to give a sense of what is being done, rather than an

exhaustive review. Adequate treatment of crystal effects, for example by molecular dynamics simulations, is certainly a prerequisite to achieving a fundamental understanding and predictive capability; however it must be acknowledged that relatively elementary considerations related to molecular structure have been surprisingly successful in producing correlations with impact and shock sensitivities. While the apparent variety of these correlations may lead to some skepticism concerning their intrinsic significance,^{25,104} most of them, even the oxygen balance formulation, are really focusing on one or both of just two key properties: the strength(s) of some particular bond(s) and the degree of uniformity of the charge distribution.

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